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(54) Title of the Invention: NONAQUEOUS ELECTROLYTE BATTERY

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Specification

1. Title of the Invention

NONAQUEOUS ELECTROLYTE BATTERY

2. Patent Claims

(1) A nonaqueous electrolyte battery comprising a negative electrode employing a light metal such as lithium, sodium and the like as an active material, a positive electrode, and a nonaqueous electrolyte in which an electrolyte is dissolved in an organic solvent, wherein said organic solvent contains ethoxymethoxyethane as the main component and said electrolyte uses any of LiCF₃SO₃, LiPF₆, LiBF₄, and LiAsF₆.

3. Detailed Description of the Invention

<Field of Industrial Application>

The present invention relates to a nonaqueous electrolyte battery using a light metal such as lithium, sodium and the like as a negative electrode active material.

<Prior Art Technology>

Nonaqueous electrolyte batteries of this type, for example, lithium batteries have a small weight and a high energy density. For this reason they are widely used in various shapes such as a tubular spiral shape, tubular inside-out shape, coin shape, and pin shape.

These batteries use nonaqueous electrolytes prepared by dissolving an alkali metal salt as an electrolyte in a nonaqueous organic solvent.

The conventional batteries typically used nonaqueous electrolytic solutions prepared by using organic solvent such as propylene carbonate, diethoxyethane, or tetrahydrofuran either alone or in a mixture and dissolving an electrolyte based on LiClO_4 in the solvent.

<Problems Addressed by the Invention>

However, in the batteries of this type, positive and negative electrodes could be short circuited during battery assembly, or a positive electrode collector and negative electrode or a positive electrode lead plate and negative electrode case could be short circuited inside the battery after it was assembled. As a result, heat was rapidly generated. Furthermore, the temperature of the assembled batteries could similarly increase under the effect of external short circuit or external heating, for example, when the battery was thrown into fire.

When LiClO_4 was used as an electrolyte, as mentioned above, there was a high danger that the increase in temperature combined with the effect of LiClO_4 in the electrolyte could lead to explosion. Moreover, for this reason, the battery had poor handleability. In particular, the degree of temperature increase inside the battery under the effect of a large current passing under short circuit conditions was especially significant in tubular spiral batteries. Therefore, the above-mentioned danger was especially high.

For this reason, safety concerns require a rapid transition to solutes other than LiClO_4 . However, the improvement of safety most often led to the degraded battery performance. Accordingly, it is desired to develop an electrolyte system which improves safety without degrading the battery performance.

<Means to Resolve the Problems>

The nonaqueous electrolyte battery in accordance with the present invention comprises a negative electrode employing a light metal such as lithium, sodium and the like as an active material, a positive electrode, and a nonaqueous electrolyte in which an electrolyte is dissolved in an organic solvent, wherein the organic solvent contains ethoxymethoxyethane (EME) as the main component and the electrolyte uses any of LiCF_3SO_3 , LiPF_6 , LiBF_4 , and LiAsF_6 .

When LiCF_3SO_3 is used as the solute, the positive electrode lead plate and battery case are sometimes corroded apparently by free fluorine contained in the solute itself or by an acid

produced by hydrolysis of the solute and a very small amount of water present inside the battery, and the corrosion adversely affects the battery shelf life.

In this case, the addition of a small amount of LiClO_4 to the above-described electrolytic solution is known to suppress effectively the above-mentioned corrosion. It is not clear what causes such anticorrosive effect, but supposedly the small amount of LiClO_4 acts as an inhibitor. Moreover, such an addition of LiClO_4 was also found to improve the discharge performance of battery.

When LiClO_4 is introduced into electrolyte, as described above, if LiCF_3SO_3 is used as the main electrolyte, then the preferred molar ratio of LiClO_4 to LiCF_3SO_3 [(molar concentration of LiClO_4 in the electrolyte)/(molar concentration of LiCF_3SO_3 in the electrolyte)] was found to be within a range of 0.05-0.2. If the ratio is below this range, then the anticorrosive effect is insufficient, and the corrosion cannot be prevented completely. On the other hand, if the molar ratio is above the range, it can lead to safety problems.

A system containing ester-type organic solvents (solvents with a high dielectric constant) such as propylene carbonate, ethylene carbonate and the like also can be used as the above-mentioned organic solvent.

Furthermore, the organic solvent can also contain at least one of dimethoxyethane, dioxolane, tetrahydrofuran or derivatives thereof. In the case of dioxolane (1,3-dioxolane), the examples of such derivatives include 2-methyl dioxolane, 4-methyl dioxolane and the like.

<Operation>

As described above, it was established that if a solvent containing ethoxymethoxyethane as the main component is used for the electrolytic solution, then a battery with high safety and practically no degradation of performance can be obtained even when solutes other than LiClO_4 are used. Furthermore, the flash point of ethoxymethoxyethane is 20°C which is much higher than that of dimethoxyethane or tetrahydrofuran that have been used as solvents for such electrolytic solutions in the past. This fact also contributes to the improvement of battery safety.

Furthermore, from the standpoint of battery discharge performance, it is preferred that LiCF_3SO_3 be used as the solute.

<Embodiment>

An embodiment of the present invention will be described below with reference to a lithium battery.

A power generation element 5 was placed into an open-end cylindrical battery case 1 made of stainless steel. The power generation element was prepared by laminating a strip-like positive electrode 2 prepared by molding a powder mixture (contained manganese dioxide as the main component and was prepared by adding a graphite powder as an electrically conductive additive and a binder thereto) and a negative electrode 3 consisting of a lithium sheet via a separator 4 made of a nonwoven fabric sheet and spirally winding the laminate. A lead terminal 6 that was led out from the negative electrode at the bottom surface of power generation element was bent to the bottom surface side of the battery via an insulating sheet 7 and spot welded to the inner bottom surface. Then, a nonaqueous electrolytic solution 8 prepared in advance was poured in the prescribed amount into the battery case. A lead terminal 9 that was led from the upper portion of positive electrode was connected to a plate-like stainless steel terminal plate 12

disposed in the opening of battery case at the inner side of an insulating gasket 10 made of a synthetic resin. As a result, a spiral-type lithium battery of CR6H type (outer diameter 14.5 mm, height 50.5 mm) having a structure shown in Fig 1 was fabricated. The nonaqueous electrolytic solution was prepared by mixing propylene carbonate and ethoxymethoxyethane at a volume ratio of 1:1, and then dissolving LiCF_3SO_3 as an electrolyte at a ratio of 0.9 mol/L.

Furthermore a number of similar electrolytic solutions were prepared in the same manner, except that LiClO_4 was added at a molar ratio to LiCF_3SO_3 within a range of 0.005-0.2. Spiral lithium batteries of CR6H size were fabricated in the same manner as described above, except that these electrolytic solutions were used.

A total of 50 batteries of each type were fabricated. The number of batteries with abnormal degradation of 0 CV was studied immediately after the fabrication (initial stage), after storage of fabricated batteries for 40 days at a temperature of 60°C, and after storage of fabricated batteries for 100 days at a temperature of 60°C. The results obtained are shown in Table 1.

Table 1

	Molar ratio of LiClO_4 to LiCF_3SO_3					
	0	0.005	0.01	0.05	0.1	0.2
Initial	0/50	0/50	0/50	0/50	0/50	0/50
After 40-day storage	3/50	1/50	0/50	0/50	0/50	0/50
After 100-day storage	6/50	1/50	0/50	0/50	0/50	0/50

The batteries that demonstrated abnormal degradation of 0 CV were disassembled and studied. Corrosion was observed on the lead plate on the positive electrode side and the separator in the vicinity thereof changed its color to dark brown. Self-discharge which is assumed to be caused by the corrosion was accelerated in the zone where color was changed, causing decrease in 0 CV.

Batteries with various amounts (molar ratios) of LiClO_4 added to LiCF_3SO_3 in electrolytic solution were fabricated (30 batteries of each type) and the number of batteries that fractured in fire was studied. The results obtained are shown in Table 2. It is clear that batteries with high safety could be obtained when the molar ratio was no more than 0.20.

Table 2

Molar ratio	0.1	0.15	0.20	0.25	0.30
Number of fractured batteries	0/30	0/30	0/30	1/30	3/30

Furthermore, batteries using electrolytic solutions with the following amounts (molar ratios) of LiClO_4 added to LiCF_3SO_3 : 0 (no addition : battery (1)), 0.0001 (battery (2)), 0.0005 (battery (3)), 0.01 (battery (4)), 0.1 (battery (5)), and 0.2 (battery (6)) were fabricated and changes in $R_{AC}(\Omega)$ during storage at a temperature of 60°C were studied. The results obtained are shown in Fig 2. The addition of LiClO_4 in a very small to small amount was confirmed to improve significantly the R_{AC} characteristic after storage.

The above-described examples related to batteries in which LiCF_3SO_3 was used as the main solute dissolved in the electrolytic solution. However, similar or better results were also obtained when LiPF_6 , LiBF_4 , or LiAsF_6 was used.

Moreover, in the above-described embodiment, manganese dioxide was used as a positive electrode active material and lithium was used as a negative electrode active material. However, the same results can be obtained when fluorinated carbon, metal oxides such as MoO_3 or CuO , and metal sulfides such as CuS or Ni_3S_2 are used as the positive electrode active materials, and another light metal such as sodium or potassium is used as the negative electrode active material.

Furthermore, the above explanation was conducted with respect to a tubular spiral battery, but similar results obviously can be obtained with batteries of other configurations such as tubular inside-out batteries, coin batteries or pin batteries.

As described above, the present invention can provide a battery of high safety demonstrating good performance.

4. Brief Description of the Drawings

Fig 1 is a cross section of the battery of the embodiment of the present invention. Fig 2 is a graph illustrating the storage characteristic of the battery of the embodiment.

[Legends]

1 – battery case; 2 – positive electrode; 3 – negative electrode; 6 – nonaqueous electrolytic solution; 12 – positive electrode terminal

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Fig 1

Fig 2

Abscissa; number of storage days (day)

1990:102160 Document No. 112:102160 Nonaqueous batteries. Shinoda, Kenichi; Yamamoto, Kohei; Harada, Yoshiro; Kitakata, Masakazu (Fuji Electrochemical Co., Ltd., Japan). Jpn. Kokai Tokkyo Koho JP 01281676 A2 19891113 Heisei, 4 pp. (Japanese). CODEN: JKXXAF. APPLICATION: JP 1988-111934 19880509.

AB Electrolytes of high-performance batteries having light metal anodes contain LiCF_3SO_3 , LiPF_6 , LiBF_4 , or LiAsF_6 and solvents mainly contg. ethoxymethoxyethane. These electrolytes contain none or small amt. of LiClO_4 and contribute to safety of batteries. Thus, an electrolyte of 0.9M LiCF_3SO_3 and 0.009M LiClO_4 in 1:1 ethoxymethoxyethane-propylene carbonate was used in Li-MnO₂ batteries. These batteries showed high storage stability at 60.degree., and none of 30 batteries exploded when thrown into fire. Batteries without LiClO_4 showed somewhat larger increase of a.c. impedance in storage, due to corrosion of metallic parts.

JP1281676A2:BATTERY OF NONAQUEOUS ELECTROLYTE

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Abstract:

Purpose: To improve safety by using either of LiCF_3SO_3 , LiPF_6 , LiBF_4 , LiAsF_6 as an electrolyte to be dissolved in a nonaqueous electrolyte of an organic solvent with its main ingredient being ethoxymethoxyethane.

Constitution: In a nonaqueous electrolyte liquid in which electrolytes are dissolved in an organic solvent, the organic solvent has ethoxymethoxyethane as a main ingredient and at least any of LiCF_3SO_3 , LiPF_6 , LiBF_4 , and LiAsF_6 is used as an ingredient. In this case, while the use of LiCF_3SO_3 is preferable from the viewpoint of the battery discharge performance, as it may corrode a lead plate on the anode side and the battery case, a small amount of LiClO_4 is added to inhibit the corrosion. The flame point of ethoxymethoxyethane is 20°C which is far higher than that of dimethoxyethane or tetrahydrofuran conventionally used in this kind of electrolyte solvent. This provides a battery of a higher safety.

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③発明の名称 非水電解液電池

②特 願 昭63-111934

②出 願 昭63(1988)5月9日

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1. 発明の名称

非水電解液電池

2. 特許請求の範囲

1. リチウム、ナトリウム等の軽金属を活物質とする負極と、正極と、有機溶媒に電解質を溶解してなる非水電解液とを備え、前記有機溶媒はエトキシメトキシエタンを主成分として有し、また前記電解質は LiCF_3SO_3 、 LiPF_6 、 LiBF_4 、 LiAsF_6 のいずれかを用いてなることを特徴とする非水電解液電池。

3. 発明の詳細な説明

<産業上の利用分野>

この発明は、リチウムやナトリウムなどの軽金属を負極活物質とする非水電解液電池に関するものである。

<従来の技術>

この種の非水電解液電池、例えばリチウム電池は、軽量で高エネルギー密度な電池であり、

筒形スパイラル形、筒形インサイドアウト形、コイン形あるいはビン形などの各種の型式のものが広く用いられている。

これらの電池では、非水系の有機溶媒にアルカリ金属塩を電解質として溶解してなる非水電解液を用いた構成が採られている。

現用の電池では、一般に、プロピレンカーボネイト、ジメトキシエタン、あるいはテトラヒドロフランなどの有機溶媒を単独または混合して用いてなる溶媒を用い、この溶媒に、 LiClO_4 を主体とする電解質を溶解させて作った非水電解液を用いている。

<発明が解決しようとする課題>

ところが、この種の電池では、電池組立中に正負極間を短絡させたり、組立後の電池にあっては電池内部で例えば正極集電体と負極、あるいは正極リード板と負極缶などが短絡した時には、急激な発熱が起こる。また、組立後に電池を外部短絡させたり、火中投入したなどの外部よりの加熱によっても同様に電池温度の上昇を

し、 LiClO_4 の作用も加わって爆発に至る危険が大きく、またそれ故、取扱性が悪いといった問題がある。特に、筒形スパイラル電池の場合は、短絡時に流れる大電流によって電池温度上昇の度合が急激であることからこの危険性が取分け高い。

このため、安全性の面から、 LiClO_4 以外の他の溶質への転換が急がれているものの、多くは安全性向上と引換えに電池性能の低下を招き、高い電池性能を維持し且つ安全性の高い電解液系の開発が望まれている。

<課題を解決するための手段>

この発明の非水電解液電池は、リチウム、ナトリウム等の軽金属を活性物質とする負極と、正極と、有機溶媒に電解質を溶解してなる非水電解液とを備え、前記有機溶媒はエトキシメトキシエタン (EME) を主成分として有し、また

含有させる際、例えば主電解質として LiCF_3SO_3 を用いる場合には、 LiClO_4 の LiCF_3SO_3 に対するモル比 $[(\text{電解液中の } \text{LiClO}_4 \text{ のモル濃度}) / (\text{電解液中の } \text{LiCF}_3\text{SO}_3 \text{ のモル濃度})]$ を 0.005 ~ 0.2 の範囲とすることが好適であることが判っている。これより少なければ防蝕効果が不十分で腐蝕を完全に防ぐことができないし、一方これより多ければ安全性の点から問題がでてくる等の理由による。

一方、上記の有機溶媒としては、アロポレンカーボネイト、エチレンカーボネイトなどのエステル系有機溶媒（高誘電率溶媒）を含んでなるものを用いることができる。

また、この有機溶媒に、ジメトキシエタン、ジオキソラン、テトラヒドロフランあるいはこれらの誘電体のうちの少なくとも1つを含むものを用いることができる。このような誘電体は、例えばジオキソラン（1,3-ジオキソラン）の場合は、2メチルジオキソラン、4メチルジオキ

ソラン等を挙げることができる。

ところで、溶質として LiCF_3SO_3 を用いた場合、溶質自体に含まれる遊離フッ素あるいは溶質と電池中の微量水分との加水分解によって生じる酸などに起因すると考えられる正極側のリード板及び電池缶の腐蝕が認められることがあり、これが電池の保存性能に影響を与えることがある。

この場合、上記の電解液において、電解質として LiClO_4 を少量添加することで、上記の腐蝕を有効に抑制し得ることが知得されている。このような防蝕効果の理由は不明であるが、少量の LiClO_4 が所謂インヒビターとして作用しているものと推定される。また、このような LiClO_4 の添加に電池の放電性能も改善されることが判った。

そしてこのように電解質中に LiClO_4 を

ソラン等を挙げることができる。

<作用>

上記のようにエトキシメトキシエタンを主成分とする電解液溶媒を用いることで、 LiClO_4 以外の溶質を用いた場合でも、電池性能の低下はほとんどなく、従って安全性が高い電池が得られることが知得された。また、このエトキシメトキシエタンはその引火点が 20℃で、従来よりこの種の電解液溶媒に使用されているジメトキシエタンやテトラヒドロフランなどに較べてずっと高く、このことも電池の安全性向上に寄与している。

また、溶質としては、電池放電性能の点から、 LiCF_3SO_3 を用いることが好ましい。

<実施例>

以下に、この発明をリチウム電池に適用した実施例を詳細に説明する。

有底円筒状でステンレス製の電池缶1の内側に、二酸化マンガンを主成分とし、これに導電剤としての黒鉛の粉末及びバインダーを加えた

重し且つ渦巻状に巻回して作った発電要素5を取納し、また発電要素底面側の負極より導出したリード端子6を絶縁板7を介して電池缶底面側に折曲しこの内底面にスポット溶接する一方、予め調合した非水電解液8を所定量注入し、更に正極上部より導出したリード端子9を、合成樹脂製の絶縁ガスカート10の内側で電池缶開口部に設置したステンレス製の皿状の端子板12に接続するなどして、第1図に示した構造の、CR6・H形（外径14.5mm、高さ50.5mm）のスパイラル形リチウム電池を作製した。尚、上記の非水電解液としては、アロピレンカーボネイトとエトキシメトキシエタンとを体積比で1:1の割合で混合した溶液に、電解質として LiCF_3SO_3 を0.9mol/l溶解させたものを用いた。

また、 LiC_2O_4 を LiCF_3SO_3 に対

分で腐蝕に起因すると見られる自己放電が促進されて0CVの低下を招いたものと考えられる。

また、電解液中の LiC_2O_4 の LiCF_3SO_3 に対する添加量（モル比）を0.1～0.30の範囲で種々変えた電池をそれぞれ30個ずつ作り、これを火中投入した時の電池の破裂数を調べた所、第2表に示した通りの結果であり、このモル比を0.20以下とすれば安全性の高い電池を得られることが判明した。

第2表

モル比	0.1	0.15	0.20	0.25	0.30
破裂数	0/30	0/30	0/30	1/30	3/30

更に、 LiCF_3SO_3 に対する LiC_2O_4 の添加量（モル比）を、0（添加なし：電池①）、0.001（電池②）、0.0005（電池③）、0.01（電池④）、0.1（電池⑤）、0.2（電池⑥）と変えた電解液を用いた電池をそれぞれ作り、これらの電池について、60℃に

ル形リチウム電池を作製した。

そして、これらの電池をそれぞれ50個ずつ作り、これらについて、電池作製直後（初度）、作製後60℃にて40日保存後、作製後60℃にて100日保存後における0CV異常劣化の数を調べたところ、第1表に示した結果を得た。

第1表

	LiCF_3SO_3 に対する LiC_2O_4 のモル比					
	0	0.005	0.01	0.05	0.1	0.2
初 度	0/50	0/50	0/50	0/50	0/50	0/50
40日経過後	3/50	1/50	0/50	0/50	0/50	0/50
60日経過後	6/50	1/50	0/50	0/50	0/50	0/50

このように0CVの異常劣化した電池を分解して調べたところ、これらの電池では、正極側のリード板に腐蝕が認められ、その近傍のセパレータが黒茶色状に変色しており、この変色部

で貯蔵した時の R_{AC} （ Ω ）の変化を調べた所、第2図に示す結果を得、 LiC_2O_4 の微量ないし少量の添加により保存後の R_{AC} 特性が著しく改善されることが確認された。

尚、以上は電解液に溶解する主溶質として LiCF_3SO_3 を用いた例であるが、その他、 LiPF_6 、 LiBF_4 、または LiAsF_6 を用いた場合にも同様ないし改善の効果が得られた。

また、上記した実施例では、正極活物質に二酸化マンガンを、また負極活物質にはリチウムをそれぞれ用いた例であるが、正極活物質として、フッ化カーボン、 MoO_3 や CuO 等の金属酸化物、 CuS や Ni_3S_2 などの金属硫化物等を、また負極活物質にはナトリウムやカリウムなどのその他の軽金属をそれぞれ用いた場合にも同様な結果が得られる。

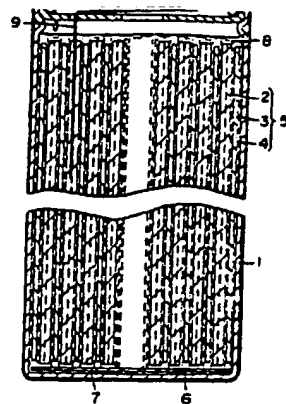
更に、以上は筒形スパイラル形電池についての例であるが、筒形インサイドアウト形、コイン形、あるいはピン形などの他の形式の電池の

以上のように、この発明によれば、電池性能が高く、また安全性の高い電池を提供することができる。

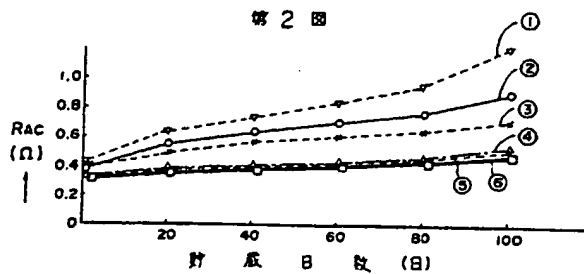
4. 図面の簡単な説明

第1図はこの発明の実施例の電池の断面図。
第2図は実施例の電池などの保存特性を示したグラフである。

1…電池缶、2…正極、3…負極、6…非水電解液、12…正極端子。



第2図



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